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Fillers and reinforcements

fillers for polymers

By Dr. Raymond B. Seymour*

Wood, one of the oldest and most widely used materials of construction, is a well known representative composite material. The properties of this product differ from those of the reinforcing cellulose fibers and the lignin resin matrix. A similar symbiotic relationship of resin and reinforcement is essential in all composites. However, the modern design engineer may select his resins and fillers from a wider variety of products. More important, he is not limited to any special ratio of components, nor to a two-component composite.

Many of wood's limitations have been overcome by the development of mechanical fabrication and joining techniques over a period of many centuries in the wood working and carpentry trades. More recently, wood has been made more versatile by forming in the presence of hot ammoniacal solutions. Presumably, these solutions reduce the intermolecular hydrogen bonding and permit slippage of the cellulose chains in the forming operation.

The anisotropy resulting from the vertical growth along the grain of wood may be reduced by plying up layers at right angles in the production of laminates, and by polymerization of monomers in situ. Composites consisting of methyl methacrylate-impreg-

nated wood are being cured commercially by irradiation.

Some fillers are inert, but there is considerable evidence that a strong attraction exists between active fillers and the functional groups on the polymer backbone. However, the International Standard Organization (ISO) uses the term "filler" to describe the non-resinous component of a composite regardless of the degree of interaction between the filler and the polymer chain.

The forces between active sites on filler surfaces and functional groups on polymer chains are weak. However, these forces are additive and become more significant with long polymer chains because of the multiplicity of these weak bonds. Some investigators have used models to predict the effects of fillers on resin properties. For example, the Nielsen theory predicts a rapid decrease in elongation as the filler concentration increases up to failure. His theory also predicts an improvement of tensile strength in accordance with filler concentration.

Other differences between the properties of filled and unfilled polymers can be readily demonstrated. Fillers reduce crystallization tendencies and solubility, and increase the glass transition temperature, hardness, and modulus of elasticity. Changes in impact resistance and coefficients of expansion of filled polymers are associated

with changes in polymer chain mobility of these composites.

The interaction between fillers and polymers in solution results in an increased viscosity. This increase may be used as a measure of the relative interaction between the polymer and the solvent or filler. Strong interactions between fillers and polymers may cause an insoluble composite substance to deposit. This phenomenon, which results when carbon black is added to rubber solutions, is termed "bound rubber" in the rubber industry.

The interaction between a polymer and a filler surface may be investigated by measuring the rate of wetting of the filler surface and the heat of absorption. Nuclear magnetic resonance techniques may be used to show a decrease in spin-spin relaxation time when silica gel is added to plasticized polyvinyl chloride. Interfacial bonds between polyester resins and fibrous glass have been investigated by infrared spectroscopy.

The principal types of fillers are classified in Table I, and some of their characteristics summarized on Table II. These fillers vary widely in availability, utility, cost, composition, and physical and chemical properties. The optimum amount of resin is the minimum required to produce a monomolecular layer on the filler surface. This limit is approached in the foundry

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shell molding process, which uses less than 3% resin to strengthen sand molds. As little as 10% resin is used with wood waste for molding large articles like desk tops and trays. However, it is customary to use at least 60% resin in most composites in order to assure good flow properties.

Most of the reinforcing fillers are high molecular weight compounds. Finely divided fillers have little effect on thermoplastics composites, but their effectiveness is increased when a small amount of crosslinking occurs. Fibrous fillers are more useful than nonfibrous fillers. A fiber length of at least 100 μ is essential for significant reinforcement of thermoplastics.

Guth has shown that the modulus (F) of a composite is a function of the volume fraction occupied by the filler (V_F) in the composite. Thus, as shown by the following equation, the modulus of the unfilled polymer (F_0) may be increased as much as 50% when the fractional free volume of the filler (V_F) is at least 20 percent.

$$F = F_0 (1 + 2.5V_F + 1.4F^3)$$

Wood products

Kraft paper may be impregnated with resin, and compression molded as laminated sheet. The impregnated paper may also be dried and chopped to yield a product that can be compression molded.

Wood flour is obtained by attrition mill or hammer mill grinding of fibrous softwoods, and to a lesser extent, hardwoods. Modern classification results in particles with uniform size which are readily wetted by resin. Dr. Leo Baekeland added wood flour to phenolic resins over half a century ago in order to reduce brittleness. This inexpensive filler reduces mold shrinkage and provides a filled thermosetting resin with good electrical properties and impact resistance. The annual production of this type of product is now about one billion pounds.

Wood flour is also used to reinforce urea resins when dark colored products are acceptable. The particle size of wood flour may be as small as 200 mesh. Fine powder yields a smooth surface finish. However, the fibrous structure is reduced by fine grinding.

Wood flour-filled phenolic molding compounds have Izod impact values of about 0.3 ft. lb./in. of notch. Wood filled plastics should not be used for extended periods of time at elevated temperatures, since the wood flour

Table I: Types of fillers for plastics

Organic Materials

- A. Cellulosic products
 1. Wood products
 - a) Kraft paper
 - b) Chips
 - c) Coarse flour
 - d) Ground flour
 1. Softwood flour
 2. Hardwood flour
 3. Shell flour
 2. Comminuted cellulose products
 - a) Chopped paper
 - b) Diced resin board
 - c) Crepe paper
 - d) Pulp preforms
 3. Fibers
 - a) Alpha cellulose
 - b) Pulp preforms
 - c) Cotton flock
 - d) Textile byproducts
 - e) Jute
 - f) Sisal
 - g) Rayon
- B. Lignin type products
 1. Ground bark
 2. Processed lignin
- C. Synthetic fibers
 1. Polyamides (nylon)
 2. Polyesters (Dacron)
 3. Polyacrylonitrile (Orlon)
- D. Carbon
 1. Carbon black
 - a) Channel black
 - b) Furnace black
 2. Ground petroleum coke
 3. Graphite filaments
 4. Graphite "whiskers"

Inorganic Materials

- A. Silica products
 1. Minerals
 - a) Sand
 - b) Quartz
 - c) Tripoli
 - d) Diatomaceous earth
 2. Synthetic materials
 - a) Wet process silica
 - b) Pyrogenic silica
 - c) Silica aerogel
- B. Silicates
 1. Minerals
 - a) Asbestos
 1. Chrysotile
 2. Amosite
 3. Anthophyllite

4. Crocidolite
5. Tremolite
6. Actinolite
- b) Kaolinite (China clay)
- c) Mica
- d) Nepheline syenite
- e) Talc
- f) Wollastonite
2. Synthetic products
 - a) Calcium silicate
 - b) Aluminum silicate
- C. Glass
 1. Glass flakes
 2. Hollow glass spheres
 3. Solid glass spheres
 4. Milled fibers
 5. Fibrous glass
 - a) Filament
 - b) Rovings
 - c) Woven roving
 - d) Yarn
 - e) Mat
 - f) Fabric
- D. Metals
 1. Steel
 2. Tungsten
 3. Titanium
 4. Beryllium filaments
 5. Molybdenum filaments
- E. Boron filaments
- F. Metallic oxides
 1. Ground material
 - a) Zinc oxide
 - b) Aluminum
 - c) Magnesia
 - d) Titania
 2. "Whiskers"
 - a) Aluminum oxide
 - b) Beryllium oxide
 - c) Magnesium oxide
 - d) Thorium oxide
 - e) Zirconium oxide
- G. Calcium carbonate
 1. Chalk
 2. Limestone
 3. Precipitated calcium carbonate
- H. Polyfluorocarbons
- I. Other fillers
 1. "Whiskers" (non-oxide)
 - a) Aluminum nitride
 - b) Beryllium carbide
 - c) Boron carbide
 - d) Silicon carbide
 - e) Silicon nitride
 - f) Tungsten carbide
 2. Barium ferrite
 3. Barium sulfate

chars when heated above 325° F.

Shell flour, obtained by grinding walnut, pecan, or peanut shells, contains lignin and furfural, which contribute to good flow properties, and cutin, a wax which provides gloss, luster, and moisture resistance. Since these fillers are spherical rather than fibrous, molded products which contain shell flour have low shear strength and lower resistance to impact than those containing wood flour.

Cellulose fibers

The smallest coherent unit of cellulose retaining characteristics of the bulk fiber is called a microcrystal. When added to liquid resins, these microcrystals produce thixotropic systems,

and thus may be used for viscosity control. Light colored moldings with fair resistance to impact are produced when alpha cellulose is used as a filler. This filler, which is obtained by the alkaline treatment of wood pulp, yields readily processed molding powders characterized by low shrinkage and low resistance to moisture. The latter deficiency may be overcome by surface treatment of this filler.

Cellulose-filled urea molding compounds are characterized by excellent arc resistance. Resin-cellulose pulp mixtures may be used as moldable preforms.

Molding compounds with medium resistance to impact are obtained by using processed cotton flock or caus-

Tabl II: Some fillers and reinforcements, and their contributions to plastics*

Filler or reinforcement	Properties Improved												
	Chemical resistance	Heat resistance	Electrical insulation	Impact strength	Tensile strength	Dimensional stability	Stiffness	Hardness	Lubricity	Electrical conductivity	Thermal conductivity	Moisture resistance	Processability
Alumina, tabular	•	•				•							S/P
Alumina trihydrate, fine particle			•				•					•	P
Aluminum powder										•	•		S
Asbestos	•	•	•	•		•	•	•					S/P
Bronze							•	•		•	•		S
Calcium carbonate ^b		•				•	•	•					S/P
Calcium metasilicate	•	•	•	•		•	•	•				•	S/P
Calcium silicate		•				•	•	•					S
Carbon black ^c		•				•	•			•	•		S/P
Carbon fiber										•	•		S
Cellulose				•	•	•	•	•		•	•		S/P
Alpha cellulose			•		•	•							S
Coal, powdered	•											•	S
Cotton (macerated/chopped fibers)			•	•	•	•	•	•					S
Fibrous glass	•	•	•	•	•	•	•	•				•	S/P
Fir bark													S
Graphite	•				•	•	•	•	•	•	•		S/P
Jute				•			•						S
Kaolin	•	•				•	•	•	•			•	S/P
Kaolin (calcined)	•	•	•			•	•	•				•	S/P
Mica	•	•	•			•	•	•	•			•	S/P
Molybdenum disulphide							•	•	•			•	P
Nylon (macerated/chopped fibers)	•	•	•	•	•	•	•	•	•				S/P
Orlon	•	•	•	•	•	•	•	•				•	S/P
Rayon			•	•	•	•	•	•					S
Silica, amorphous			•									•	S/P
Sisal fibers	•			•	•	•	•	•				•	S/P
TFE-fluorocarbon						•	•	•	•				S/P
Talc	•	•	•			•	•	•	•			•	S/P
Wood flour			•		•	•							S
Altered novaculite	•	•	•	•		•	•	•			•	•	S/P

*The chart does not show differences in degrees of improvement; calcined kaolin, for example, generally gives much higher electrical resistance than kaolin. Similarly, differences in characteristics of products under one heading, such as talc (which varies greatly from one grade to another and from one type to another), also are not distinguished.

a—Symbols: P—in thermoplastics only; S—in thermosets only; S/P—in both thermoplastics and thermosets. b—in thermosets, calcium carbonate's prime function is to improve molded appearance. c—Prime functions are imparting of UV resistance and coloring; also is used in crosslinked thermoplastics.

tic-purified cotton linters. Cotton flock-filled molding powders are characterized by high bulk factor, and low moisture resistance. The former characteristic may be modified by blending with wood flour; the latter is improved by surface treatment of the flock. These molded products have impact resistance as high as 0.6 ft. lb./in. of notch.

Products with still higher impact resistance values are obtained by the resin impregnation of small pieces of cotton cloth (macerated fabrics).

Jute fibers, yarn and fabric have been used for reinforcements in phenolic composites. These fabrics have low strength, but this deficiency is

overcome in part by using parallel jute fibers. Molding powders with moderate resistance to impact are produced from chopped fibers from the agave shrub. These sisal fibers have diameters of 0.005–0.020-in. and are 2–5 ft. long.

Rayon fibers are produced by the coagulation of viscose solutions after they have been extruded as filaments through spinnerets. Rayon may be used both as flock and as yarn. The impact resistance of the molded product is a function of its fiber length.

Lignin is the natural binder for cellulose in wood. A product containing this type filler may be obtained by grinding the bark of Douglas fir trees,

or by extending wood flour with a derivative of lignosulfonic acid. Steam hydrolysis of wood also yields a filler which has fair flow properties because of the lignin present. All of these dark colored fillers have been used with resins to produce molding powders. Since the lignin contributes to flow, less resin is required.

Synthetic organic fibers

Nylon is also available as flock, filament, and chopped fabric. Being thermoplastic, it flows at temperatures used in molding phenolic resins. Thus considerable shrinkage take place during molding. Gears and other products molded from nylon-filled phenolic res-

in maintain excellent abrasion and wear resistance.

Chopped fibers and filaments of polyester and polyacrylonitrile are used to reinforce allylic resins. Nylon-filled thermosetting resins are being used as ablative materials.

Carbon

Carbon black is the principal filler for all types of elastomers. It is also used as a pigment and filler for polyethylene, polypropylene, polyvinyl chloride, phenolic, furane, and epoxy resins. Carbon black reduces the sizes of crystallites and improves resistance to stress cracking and ultraviolet degradation of polyolefins. This effect is more readily demonstrated with filled crosslinked polymers.

Reinforcing carbon black is made up of crystallites consisting of layers of carbon atoms. *Channel blacks* with particle sizes ranging from 200 to 300A are produced by burning natural gas in a limited supply of air, and allowing the products to deposit on cold metal surfaces.

Furnace blacks with particle sizes ranging from 300 to 800A are produced by burning gas or oil in a limited supply of air, and removing the products by centrifugation or electrostatic precipitation. Thermal, acetylene, and lamp black and ground petroleum coke are coarser than the more widely used reinforcing blacks.

It has been observed that a significant increase in modulus occurs when crystalline compounds with a β -naphthyl group are added to elastomers. It has been proposed that the alignment of these crystals with polymer backbones is related to a comparable effect observed in carbon filled filaments.

Carbon filaments have been produced by the pyrolysis of organic fibers, such as rayon at 2552-3092° F. Removal of surface moisture is essential for the production of high strength resin composites. The composition and properties of these fibers may be varied widely by the incorporation of such additives as metal salts before extruding the filaments.

Graphite filaments may be used directly, or they may be woven into broad fabrics. These filaments are characterized by high tensile strengths at high temperatures (4800° F.) The resistance to oxidation and the interlaminar strengths of graphite fiber composites have been increased by a so-called "whiskering" process. In this

Table III: Physical properties of typical reinforcements

Material	Specific gravity	Melting point, ° C.	Tensile strength, $\times 10^3$ p.s.i.	Modulus of elasticity, $\times 10^4$ p.s.i.
Aluminum	2.7	1220	90	11
Aluminum oxide	4.0	3780	1000	76
Aluminum nitride	3.3	3990	100	50
Asbestos	2.5	2770	200	25
Beryllium	1.8	2343	250	44
Beryllium oxide	3.0	4650	75	51
Boron	2.6	3812	500	60
Boron carbide	2.5	4400	500	65
E-glass	2.6	2400	500	11
S-glass	2.5	3000	700	13
Graphite	1.4	6600	250	37
Molybdenum	10.2	4370	200	52
Nylon	1.2	4880	120	0.4
Polyester	1.4	480	100	0.6
Quartz	2.2	3500	1000	10
Silicon carbide	3.2	4200	100	1000
Silicon nitride	3.2	3450	50	55
Steel	7.9	2920	600	30
Tantalum	16.6	5425	90	28
Titanium	4.7	3035	280	17
Tungsten	19.3	6170	620	58
Tungsten carbide	15.7	5200	106	104

process silicon carbide whiskers are grown on all available surfaces of the graphite strand bundles.

The high temperature curing of laminates is facilitated when one or more graphite laminate layers are utilized as internal resistance heating units. The addition of coke to polytetrafluoroethylene produces an inexpensive antifriction composite. Ground coke is also used in plastics cements.

Silica products

Sand, quartz, tripoli, and diatomaceous earth are naturally occurring forms of silica which differ in particle size, degree of crystallinity, and hardness. Large volumes of graded silica sand are used with small proportions of resin in the shell molding process, and in the resin cements. Sharp silica sand often is spread over uncured surfaces of resin cements to provide abrasive qualities on the surface.

Naturally occurring quartz has been used as a filler with phenolic and epoxy resins to provide ablative insulators for nose cones, space capsules, and rocket motors. Quartz has also been used to study the effect of surface treatment of siliceous fillers on their adhesive properties.

Diatomaceous earth, infusorial earth, or fossil flour is obtained from deposits of skeletons of organisms called diatoms. The commercial products are obtained by heat treatment which removes much of the water from the naturally occurring substance. The use of this type filler in polyure-

thane foams provides improved compressive strength and reduces shrinkage.

Silica fillers are also produced by wet and pyrolytic processes. *Amorphous silica* is obtained by precipitating silica from a solution of sodium silicate. In one commercial process, calcium chloride is added and the calcium silicate produced is treated with hydrochloric acid. In other commercial processes, the sodium silicate solution is acidified by such gaseous acids as carbon dioxide or hydrogen chloride.

Silica fillers contain "free water," which is reversibly removed at 212 to 392° F., and "bound water," which is irreversibly removed at 1652-1832° F. Much of the reinforcing properties of these light colored fillers is associated with active silanol surface groups which are destroyed at elevated temperatures.

Pyrogenic silica is obtained by flame or fume processing of silicon tetrachloride in the presence of hydrogen and oxygen. Pyrogenic silica has a particle size average of 0.015 microns, low free moisture content (1%), and a large external surface area (200 sq. m./gm.).

Asbestos products

Asbestos is a naturally occurring fibrous hydrated magnesium silicate. Most of this filler is of the chrysotile fibrous serpentine type. Amosite, anthophyllite, crocidolite, tremolite, and actinolite are included in the amphibole group. Crocidolite asbestos has

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been used for the fabrication of filament-wound equipment, and anthophyllite has been used to reinforce thermoplastics.

Composites containing asbestos are characterized by good resistance to corrosion, heat, rot, mildew, and weather. Asbestos in the fibrous form and as "floats" has been used as filler with a wide variety of resins to produce molding compositions, mastics, floor tile, and troweling compounds. (See also the article "Asbestos reinforcements and fillers, p. 586.)

Fluoroplastics

Oriented TFE-fluoroplastic fibers dispersed in acetal resin create a plastic that combines the properties of both materials. Advantages claimed include no need for lubrication, low dynamic friction, high PV values, outstanding chemical resistance to organic solvents, an upper service limit of 185° F. in continuous operation, and very low static or breakaway friction. Finely divided fluoroplastics are also being used as lubricants in thermoplastics and thermosets. The wear life has been increased manifold, and temperature limitations have been raised by the addition of fluoroplastic particles to these formulations. Glass-filled polytetrafluoroethylene composites are being used as self-lubricating bridge pads.

Metals as fillers

Metal powders such as bronze or aluminum may be added to acetals or nylon to produce conductive moldings that may be plated with metals. Polymers having high percentages of zinc are useful as protective coatings. Polyolefins containing heavy metal powder, such as lead, are used as neutron and gamma ray shields.

Epoxy resins with large quantities of finely divided metals, such as aluminum, are used to cast forming tools and for producing metal cements and coatings. Reinforcements of beryllium, chrome, molybdenum, niobium, stainless steel alloys, tantalum, titanium, and tungsten have been added to resins to produce heat resistant composites. Tungsten wire is also used as a support for other reinforcements like boron.

Glass as a filler

Glass is available in "C", "E", and "S" types. The "C" glass, which has a low soda content, is characterized by resistance to all acids except hydroflu-

ric. The "E" glass is a lime-alumina-borosilicate glass. The "S" glass has a high modulus and high tensile strength at 1600° F. (The use of fibrous glass in plastics is treated in detail in the article "Fibrous glass reinforcements," p. 592.)

Tests by the Underwriters Laboratories (UL subject 94), and ASTM flammability tests (D-635-63) have shown that filled composites have improved flame resistance. Many fibrous glass-filled thermoplastics are acceptable while the unfilled resins do not pass these flame resistant tests.

Glass flake* in protective coatings improves plastics corrosion resistance and forms an impermeable barrier to vapors. Available today are super-thin flake and a heavier flake which costs substantially less.

In epoxy, polyester, and urethane flooring and wall surfacing, glass flakes give a tough surface with excellent chemical and abrasion resistance. Colored flake serves as a decorative element.

Glass granules*: Glass in granular form adds excellent non-skid, non-slip properties to epoxy, polyester, or urethane coating systems for ship-board deck and industrial floor use, and are specified by the U.S. Navy for use in skid-proofing aircraft carrier flight decks. Prime quality granules, available from some manufacturers, are controlled in production to be exceptionally clean, and to be cubic or rectangular, having no sharp edges or points (unlike scrap ground glass).

Solid glass spheres*: Soda lime glass in solid spherical form—smooth, transparent, hard, lightweight—has proved to be an effective reinforcement/filler in both thermoplastics and thermosets. Available in diameters of 2-500 microns, it reinforces the mechanical, electrical, chemical, and thermal properties of base resins, often at cost savings (diameters of 6-50 microns are most popular with plastics).

The perfect spherical shape and smooth surface keep resin viscosity low, permitting high loading of spheres and good mold flow. Spheres set up more predictable and uniform stress patterns in moldings than do irregular-shaped particles or short fibers, with resultant gains in physical properties. The spheres improve flexural strength and modulus, and yield smooth, reinforced surfaces, corners, and edges in

molded parts. Addition of glass spheres to a resin mix decreases the burning rate of a molded part. Due to the coating of spheres with a coupling agent, resin-glass bond is improved, with gains in tensile strength and other physicals.

In thermoplastics, solid glass spheres have been used successfully as reinforcement/filler in ABS, nylon, and vinyl. Their biggest use to date has been in nylon, in which the spheres improve tensile strength, reduce elongation, sharply increase flexural modulus, and almost triple compressive strength compared to nylon resin alone.

It was in thermosets that glass spheres got their start as a reinforcement/filler for plastics. They are used in epoxy, polyester, and phenolic resins. In polyester, they have made possible a low viscosity, highly loaded, reinforced polyester hand layup system having physical properties equal to those of high pressure moldings. Addition of glass spheres to glass fiber-epoxy laminates has proved to increase flexural strength and modulus substantially without significant loss of other properties. Replacing quartz as a filler, glass spheres increase modulus and flexural, tensile, and impact strengths.

The combination of high loading, low specific gravity, and low price permits molders to effect sizable cost savings while improving physical properties of molded parts.

Cellular glass modules with multiple closed cells have also been used as resin fillers. Low density syntactic foams with controlled specific gravity may be obtained when *hollow glass spheres* are added to resinous composites.

Calcium silicate*

Naturally occurring calcium metasilicate (wollastonite) has been used in high concentrations for years in thermosetting molding compounds (polyesters, epoxies, phenolics, etc.), in paints (oil and water-based exterior types, alkyd flats, interior latex systems, primer surfaces, etc.), and in ceramic bodies. More recently, the general growth of mineral reinforced systems has resulted in the discovery of far-ranging functional and economic benefits justifying use of wollastonite in thermoplastics and enhancing its thermosetting versatility.

Basically, wollastonite is a high-melting acicular mineral available in grades ranging from very fibrous to

finely divided. The general properties, which are of benefit to almost all plastics systems utilizing wollastonite, include low cost, high uniformity, purity and brightness, resin compatibility, low oil and moisture absorption, chemical resistance, mechanical reinforcement, and outstanding electrical and thermal insulation character. For specific applications, wollastonite imparts the following:

In epoxies: At loadings from 50% in encapsulating and potting compounds, dielectric constants from 2.2 and 2.8 are obtainable along with low moisture absorption; low, stable viscosities; reduced peak exotherm; less heat shock during cure; inhibition of crack formation; increased pot life; good flexural, tensile, and compressive strengths; good chemical resistance; and an excellent level of impact resistance.

In polyolefins (particularly polypropylene): Wollastonite provides distinct advantages in electrical insulation. Dissipation factors and dielectric constants at one megacycle have been recorded at 0.00055 and 2.75 respectively at 40% loadings in polypropylene, and 0.00097 and 3.20 at loadings as high as 60 percent. Corresponding results have been obtained at 60 cycles, and recent studies reported with low density polyethylene have revealed excellent electrical stability during aging at 120° F., and 97% relative humidity. For the mechanical reinforcement of polypropylene, acicular grades of wollastonite produce higher Izod impact strengths than many other mineral fillers. Together with low cost, this allows the processor to use high filler loadings (45-60%) which, in turn, achieve high flexural modulus properties at lower total and price-volume raw material costs than do corresponding volumes of other systems at lower loadings.

These properties, together with low values for heat distortion and moisture absorption, processing ease, colorability, and the other general characteristics described above, account for the continually increasing commercial popularity of wollastonite for use in polyolefins.

In PVC: Wollastonite shows particular value in such vinyl compounds as homogeneous and asbestos-filled floor tiles, vinyl sheeting, and vinyl plastisols. Depending upon the specific properties of major importance to the application at hand, different grinds at different levels of particle size, uni-

* Material on glass flake, granules, and solid sphere contributed by James R. Ritter, Director of Research, Potters Bros. Inc., P.O. Box 14, Camden, N. J. 07072.

* By Dr. Edwin B. Carton, Cabot Corporation, 125 High St., Boston, Mass. 02110.

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formity, and acicularity are preferred. Two areas that make possible cost saving in vinyl formulas are the unusually low plasticizer absorption of wollastonite and its very slight contribution toward opacity. The former permits high loadings at reduced raw materials costs, while the latter enables the compounder to achieve equal mass tones, which reduce the requirements for expensive color pigments.

Optical brightness; light, weathering, heat, and processing stability; rapid dispersibility; low shrinkage and moderate reinforcement properties add to the versatility and effectiveness of wollastonite in filled vinyl systems. Additionally, when utilized in vinyl plastisols, low and uniform viscosities may be maintained even at high filler loadings. As in other plastics systems, the various grades of wollastonite offer excellent electrical insulating characteristics combined with low moisture absorption and ease of dispersion in conventional equipment.

In nylon: Wollastonite is used in nylon molding compounds because of low moisture content, light color, brightness, dimensional stability, and reinforcement.

In phenolics: Favorable mechanical and electrical properties—including tensile strength, modulus of rupture, compressive strength, Izod impact, and electrical loss factors—have been reported for wollastonite-filled phenolic molding powders.

In polyesters: High concentrations of wollastonite are used in polyester roofing cements and molding compounds based upon low measurements for water absorption, dielectric constant, and viscosity at high loadings, as well as upon the aesthetic optical properties of surface smoothness and whiteness.

In paints (vinyl acetate and alkyd): White house paints containing wollastonite maintain high brightness after long exposure at low and normal zinc oxide levels, and colored house paints show excellent tint retention. Wollastonite is used commercially as an extender pigment in all types of paints, primarily because of its low oil absorption, brilliant whiteness, and the mechanical reinforcement imparted by its acicularity. In some applications compromises must be exercised, because if too acicular a grade is chosen improved mechanical reinforcement may be offset by a negative visual factor known as the "cross-brushing" effect. Where this factor is

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important, more finely divided grades of wollastonite are indicated. In addition, wollastonite-filled paints improve leveling, control pH and pH drift in emulsions, reduce film sheen, decrease wetting agent requirements, improve scrub resistance, and show excellent can stability.

In other resins: Wollastonite has been recommended for commercial use in various elastomeric systems (i.e. fluorocarbons, SBR rubbers, etc.) where advantage may be taken of its good balance among low values for cost, dielectric loss factor and moisture absorption, excellent aged electricals, and retention of mechanical properties (particularly at elevated temperatures), and/or processing safety without scorching or excessively increasing hardness.

Some use is made of wollastonite as a non-moisture-absorbent filler in melamine tableware, primarily because of its stain resistance, and in urethanes. Additional applications are being tested and/or commercialized by producers and processors of other plastics including polystyrene, ABS, chlorinated polyethylene copolymers, crosslinkable polyethylene, etc.

Although the semi-reinforcement effects of wollastonite occur because of the needlelike crystal structure and may be enhanced by the use of special fibrous grades, and although its use is specifically indicated in plastics components and coatings where high electrical and weathering resistance and low moisture absorption are desired, these properties may be enhanced further by coating the surface with a coupling agent such as an organosilane. The effectiveness of various commercial silane coupling agents, with wollastonite has been demonstrated in

a variety of resins. Published tests with a number of fillers have shown that wollastonite/silane systems impart equal functional properties at lower overall raw material costs, or improved properties at equal costs, or both. Proper silane treatment levels for one-monolayer additions vary with chosen grade of wollastonite, but may be estimated by assuming average surface area of wollastonite to be 1.5 sq. meters/gram.

Fumed colloidal silica*

Fumed colloidal silica—also called pyrogenic silica—is an amorphous synthetic made by hydrolyzing silicon tetrachloride in an oxygen-hydrogen flame at high temperature. It is distinguished by purity in excess of 99.8% and extremely fine primary particles (12 mμ average) that are loosely agglomerated. The available external surface area in one gram of the material may be varied by production techniques to as high as 380 m².

Functions in either thermosetting or thermoplastic systems generally are 1) to thicken the resin and improve thixotropy, 2) to reinforce a resin, 3) to suspend pigment and filler, 4) to prohibit blocking of plastics film, 5) to improve flow properties of dry powders, 6) to elevate electrical characteristics of cable compounds.

Although dispersion methods, the polarity of the system, and other parameters influence efficiency, relatively small concentrations usually suffice to achieve the desired results.

Among 12 grades now on the market are post-treated grades having extremely high surface area (for better

* Material supplied by Degussa Inc., 2 Penn Plaza, New York, N.Y. 10001.
1—Degussa process.

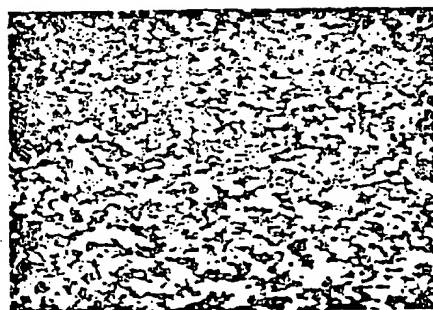


FIG. 1: Electron micrograph of fumed silica in a cured, unsaturated polyester resin.

efficiency), modified particles (for thickening polar systems), hydrophobicity (for moisture resistance), and a slight amount of colloidal aluminum oxide on particle surfaces (for anti-blocking of plastics materials).

Nepheline syenite*

A naturally occurring sodium potassium aluminum silicate of exceptional uniformity, nepheline syenite, when produced in finely ground form exhibits outstanding dry brightness, low vehicle demand, and extremely low tinting strength. Currently it is most widely used as a filler in both rigid and flexible PVC resins, where its very slight contribution to opacity is almost unique. Near transparency can be achieved, and savings are possible because requirements for coloring pigments can be reduced and high loadings are possible.

Nepheline Syenite in epoxy castings and polyesters (including car patch compounds) is extremely easy to wet and disperse, and high loadings are possible. Nepheline syenite is reported to contribute to excellent overall electrical properties, and to be outstanding in the reduction of the dissipation factor.

Barium sulphate†

Chemical inertness, low water solubility, and high specific gravity are properties that recommend barium sulfate as a filler for many plastics. At 4.4 specific gravity it is heavier than most white fillers, and is therefore used where high density is desired. Also, plastics containing it are opaque to X-rays. Natural barium sulfates hav-

* Material on nepheline syenite supplied by American Nepheline Corp., subs. of Industrial Minerals of Canada Ltd., Suite 6, 11 W. Cooke Rd., Columbus, O. 43214.

† Material on barium sulphate by Arthur K. Woernle, Technical Service Coordinator, Minerals, Pigments, and Metals Div., Chas. Pfizer & Co. Inc., 640 N. 13 St., Easton, Pa. 18043.

Table IV: Synthetic colloidal silicas and their properties

	Hydrogels	Aerogels	Precipitated	Fumed
Purity, % SiO ₂	96.5-99.7	90-96	85-87	>99.8 ^a
Loss on ignition at 1000° C., %	0.6-13.0	4.0-5.5 ^a	10.5-12	<1.5
Loss on ignition at 105° C., %	—	—	6	<1.5
Bulk density, lb./cu. ft.	4.8-34	2.5-6.0	4-12	2.5-6.0
Surface area BET, m ² /g	230-830 ^a	130-280 ^a	30-325 ^a	50-400 ^a
Primary particle size, millimicrons	10-20	10-20	16-22	5-50
Average agglomerate size, microns	2.9-11	2.0-5.0	30	NA ^b

1—Loss on ignition is determined at 600° C.

2—Surface area is partially internal.

3—Highest degree of purity—lowest content of electrolytes.

4—Surface area is all external.

5—Agglomerate size cannot be determined as primary particles are only loosely associated.



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ing selected particle size distributions are finding use as a filler in polyurethane foam¹, where they impart increased density, increased load bearing properties, improved processing, and improved drape and hand. The low vehicle demand of natural barytes together with the previously listed properties make it an ideal compound in plastisol compounds, particularly for sealing rings in food jar covers.

Kaolin clay*

Kaolin clay is used as a filler or extender in several types of thermoplastic and thermosetting systems. It is used alone in many applications, and in combination with other mineral fillers to give special effects. Kaolin is sometimes used to reduce the overall cost of a formulation, but in many cases, it is incorporated entirely for its contribution to the performance of a compound.

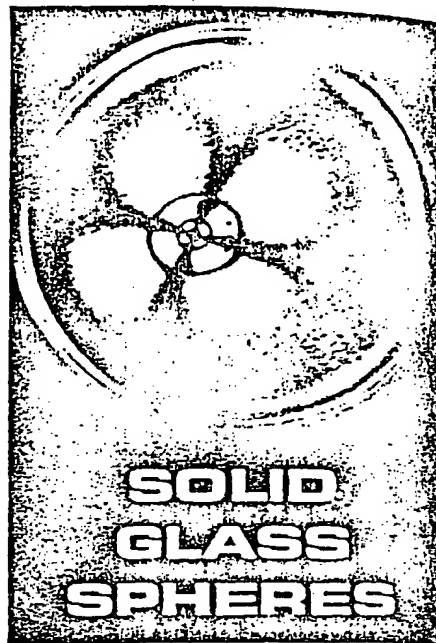
In polyester resin compounding, kaolin clay is an important ingredient in premix, preform, and mat moldings made by the matched metal mold technique. In premix compounds, kaolin and other fillers make it possible to control the consistency and moldability of the compound, and kaolin in particular contributes to chemical resistance, low water absorption, good electrical properties, etc. Kaolin is frequently combined with both lower and higher oil absorption fillers in premix compounds to yield properties that are not obtainable with a single filler system. Bulk molding compounds (BMC) are similar to conventional premix compounds, but they employ a chemical thickening agent to develop high viscosity. However, kaolin and other fillers are still required in BMC to develop the optimum properties of this new system. Normally, kaolin loadings vary from 10 to 55% of the total formula, depending on molding requirements and performance required from the finished product.

In preform and mat molding, kaolin fillers give excellent protection against crazing, and generally provide higher reverse impact values than other low cost fillers. Surface smoothness and appearance are also improved when kaolin is used as the filler. In general, coarse particle-size kaolin is preferred in preform and mat molding because it does not increase the

¹—See U.S. Patent No. 3,298,967.

* Material on kaolin clay by John C. Nease, Research Supervisor, Minerals and Chemicals Div., Engelhard Minerals and Chemicals Corp., Menlo Park, Edison, N. J. 08817.

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resin-filler viscosity as much as finer particle clays. However fine particle size clays offer more opacity, and as a result tend to "hide" or cover up the glass fibers better than coarse clays. Also, the water classified clays exhibit both better color and better uniformity of properties than air-floated clays.

Sheet Molding Compounds (SMC) also employ a chemical thickening agent, and kaolin fillers are preferred over other fillers in this system because they provide chemical resistance and better reverse impact values. Kaolin is also suggested as the filler for other new low shrinkage polyester resins, and for the extremely low viscosity vinyl ester resins. Kaolin loadings as high as 60% have been used in vinyl ester systems, but conventional preform and mat compounds and SMC normally employ 20 to 45% clay. It is not common practice to use more than one filler in these systems because the flow requirements are not as demanding as in premix systems. However, there is some indication that the SMC products may in the future ultimately employ two types of fillers.

In thermoplastics, calcined kaolin is widely used as a filler in vinyl wire insulation compounds. Calcined clay dramatically improves the insulation resistance of plasticized vinyl. While far from conclusive, there is evidence that indicates the clay functions by an ion exchange mechanism. At the same time, the clay may also function by ion absorption and acid acceptance. The clay loading can vary from about 5-30 phr, although 10-15 phr is a more realistic loading. Resistance increase is less pronounced above a loading of 20 phr, and the relatively high oil absorption of the clay produces a marked stiffening effect. This type of clay also provides low water absorption in PVC. Because it is not a highly calcined clay, the color is cream rather than white.

Commercial kaolins are available in a variety of forms and particle sizes. The properties of air-floated clays are controlled by the deposit from which they are mined, since the air flotation equipment is not capable of close particle size fractionating. Water-classified clays, on the other hand, offer close particle size control as well as control of color, brightness, pH, and impurity content. Although kaolin particles occur naturally in a wide distribution of sizes, the average particle size of commercial products varies only from ap-

proximately six microns to less than 0.5 micron.

Calcined clays are thermally treated to remove the water of hydration. This treatment alters the crystal structure of the product and changes many of the other characteristics such as brightness, particle size, hardness, and oil absorption.

Calcium carbonate*

Two major categories embrace calcium carbonates used as fillers for plastics: natural ground limestone, and precipitated grades of calcium carbonate. Ground limestones—dry or wet ground—range from a minimum of 1/2 micron to 44 microns in particle size, the latter being the upper practical limit for a pigment grade. Dry ground types usually are over 20 microns in particle size; wet ground are less than 20. Specific grades are available with surface treatment.

Precipitated calcium carbonates are manufactured by several processes, the most common being soda ash-calcium chloride, ammonium carbonate-calcium chloride, and carbonated milk of lime reactions. Other sources are treatment of hard water with soda and of causticized waste in paper plants. Particle sizes range from ultra-fine (0.05 micron) up to 10 microns. Precipitated calcium carbonates also are available with several types of organic coating agents such as resins, fatty acids, and dispersants.

Both precipitate and natural ground limestones are higher in whiteness and brightness than other types of fillers and these are major factors in their selection.

Most plastics compounders use precipitated grades of calcium carbonate, wet ground limestone treated for low oil-plasticizer absorption, or uncoated larger particle grades (up to 10 microns). Wet ground limestones less than 20 microns in particle size also are popular; again they are usually selected for low oil-plasticizer absorption.

Because of their low oil-plasticizer absorption and particle size uniformity, both types offer easy processing, little or no abrasion of equipment, and possibility of employing high levels of filler. These types also have little or no effect on the physicals of thermoset resins, except at extremely high load-

ings. In thermoplastic resins they reduce physicals in proportion to amounts used, but to a lesser degree than the coarser dry ground limestones.

In PVC: Calcium carbonate is the filler most widely used in PVC compounds. Favorable raw material cost, ready availability, and a wide range of particle shapes and sizes are major considerations. Although pound/volume cost reduction is the major consideration, calcium carbonates are used in PVC compounds for specific performance characteristics.

Precipitated grades in the five to 10-micron range and wet ground types are the most popular. These grades have relatively low oil-plasticizer absorptions, which permits high filler loading levels without excessive use of plasticizers. Homogeneous PVC floor tile, and extruded and calendered products are areas for these grades. Level of calcium carbonate might run from 5-100 PHR depending on hardness, opacity, and physicals desired. Precipitated grades with fatty acid type coatings are often used in extruded vinyl compounds, both rigid and flexible. The fatty acid coatings act as lubricants, and to a lesser degree, stabilize the compound. Because of the coatings, smoother surfaces on extruded products can be predicted as well as higher extrusion rates and less die wear.

Size dictates applications: Dry ground limestones of over 20 microns are generally preferred in vinyl asbestos floor tile. Because of larger particle size, they have extremely low oil-plasticizer absorption and permit high filler loading levels. The larger particles of calcium carbonate, plus the irregularly shaped asbestos fragments, compact into the hard non-porous surfaces generally desirable in vinyl asbestos floor tiles.

Precipitated calcium carbonates in the 0.10 to 0.25-micron range impart considerably more brightness and hiding power than the larger particle types. They often are used in white PVC compounds to supplement the more expensive titanium dioxide pigment. The high hiding power of these grades also contributes to more efficient ultraviolet screening action.

The ultra-fine precipitated grades in the area of 0.05 to 0.07 microns are used sparingly in PVC compounds. Their large surface areas contribute to increased plasticizer absorption, with consequent higher raw material cost

* Material on calcium carbonate by Philip F. Woerner, Manager, Technical Department, Specialty Chemicals Division, Diamond Shamrock Corp., 300 Union Commerce Bldg., Cleveland, O. 44114.

and added processing problems. Outstanding characteristics imparted by these ultra-fine types are mar resistance plus low whitening on flexing. Higher surface gloss is also possible with ultra-fines. Homogeneous high grade PVC floor tile is a major end use for ultra-fine grades.

PVC plastisols demand easy mix-in type calcium carbonates, and precipitated grades in the 0.5 to 10-micron range are preferred, with wet ground limestone employed to a more limited extent. Larger particles (over 10 microns) constitute a greater problem in plastisols because of settling possibilities and the possibility of creating irregular surfaces. Small amounts of ultra-fines, both coated and uncoated, are used to develop thixotropic plastisols. But they must be properly dispersed to develop the required body.

In the development stage, is an easy dispersible grade of ultra-fine precipitated calcium carbonate. To obtain desired plastisol viscosity and thixotropy, simple mixing on a Hobart type mixer or its equivalent is sufficient. This relatively agglomerate free ultra-fine produces extremely smooth plastisol films with excellent physical properties.

In polyesters: Polyester compounding has now become a large use area for calcium carbonate fillers. As in PVC compounding, calcium carbonates offer favorable raw material cost, availability, various particle sizes and shapes, and good color characteristics.

The easy mix-in types of precipitated calcium carbonate and wet ground limestone are usually preferred. Low oil-plasticizer absorption grades permit higher filler loading levels. Resin coated precipitated calcium carbonate is extremely popular because of its excellent dispersibility, plus its affinity for polyester resins. The resin coated grade imparts considerably smoother surfaces to laminates than do uncoated grades.

Filler loading levels in compression molded laminates average about 35% of the total weight of mix. Physicals, such as impact and flexural strength, increase with the use of calcium carbonate up to 50% by weight, then start to drop off rapidly. Besides increasing impact and flexural strengths, the filler also lowers lb./volume cost, improves surface smoothness and hardness, increases heat resistance, and reduces mold shrinkage.

In hand layup operations, calcium carbonate filler is usually less than

30% of the weight of mix. Excessive use of filler may prevent adequate penetration, creating resin-starved areas and weak laminates.

Premix polyester molding employs higher levels of filler to develop increased stiffness or body. Low oil-plasticizer absorption precipitated calcium carbonates and wet ground limestones usually are employed. Usually these are employed alone; sometimes they are modified with finer particle size precipitated grades in the intermediate and ultra-fine ranges.

Polyester gel coats may contain calcium carbonate up to 25% of the total mix. Good dispersibility is essential because low spraying viscosities are mandatory. Outstanding properties which calcium carbonates contribute to gel coats are brightness and whiteness, hiding power, smoothness, better adhesion to substrate, and improved spraying characteristics. Limited amounts of ultra-fine precipitated calcium carbonates are also used in gel coats, where they function as suspension agents and reduce sag.

In epoxies: The lower oil-plasticizer absorption grades of precipitated calcium carbonate and wet ground types of ground limestone are preferred in epoxy molding compounds. Resin-coated grades of precipitated calcium carbonate are especially desirable because of their greater affinity for epoxy resins, which permits higher levels of filler and easy mix-in in the preparation of the compound.

Encapsulating and potting compounds contain filler loadings consistent with pourability. The filler reduces compound shrinkage to a minimum, providing increased impact strength, greater resistance to heat, and lower coefficient of thermal expansion. Fillers in encapsulating and potting compounds will usually total at least 50% or more of the total mix.

Epoxy adhesives also contain calcium carbonate fillers in a range from as low as 5% to as high as 50%, with the average about 20% of the total weight of mix. The most important contributions of fillers in adhesives are increased tensile and shear strength, minimum loss of adhesive in porous substrates, and increase in modulus. Secondary considerations in their use are control of shrinkage, increased resistance to heat, and reduced thermal expansion. Resin coated precapsulated grades in the 05-2 micron range are preferred.

Epoxy resin laminates are com-

pounded along the lines of polyester resin laminates, usually averaging about 30% calcium carbonate on total weight of mix. Again resin coated, precipitated calcium carbonate is preferred, although some of the finer grades of wet ground limestone are employed. Low oil-plasticizer absorption of these grades permits the utilization of higher loadings with good flow properties.

In polyolefins: Limited amounts of calcium carbonate fillers are being used in polyethylene and polypropylene compounds where they impart hardness, stiffness, and opacity as well as reduce cost. Filler preference is generally ultra-fine precipitated calcium carbonate, larger particle precipitated grades, and wet ground limestone. Ultra-fine grades are used in amounts up to 30% of the total mix weight.

In phenolics: In addition to lowering compound cost, calcium carbonate fillers improve the physical properties of molded phenolics. Impact strength and heat resistance are improved, and mold shrinkage decreased. Resin-coated precipitated calcium carbonate is used because of its affinity for phenolics, and because of the consequent improvement in physicals and surface smoothness; wet and dry ground limestones also are used. The amount of calcium carbonate filler in phenolic compounds is usually more than 20% of the total mix, and often goes as high as 70 percent.

In polyurethane foams: Both precipitated and wet ground limestones are being used in rigid and flexible foams in order to increase volume and lower compound cost. In both types, cell structure is related to particle size uniformity and shape. Resin coated intermediate particle size precipitated calcium carbonates with excellent mix-in characteristics and a low moisture content, and are generally preferred. Low moisture dry ground limestones are also used in both rigid and flexible foam.

Altered novaculite*

Altered novaculite (lower member of the upper novaculite) is believed to be an alteration of the lower novaculite (blue-white hard Arkansas stone). Both the lower and the upper novaculite are typically 99.5% quartz (SiO_2).

Altered novaculite has the basic

* Material on altered novaculite by J. E. Moreland, Sales, Malvern Minerals Co., P.O. Box 1246, Hot Springs, Ark. 71901.

hardness of quartz, but lacks the usual violent abrasive characteristics of SiO_2 , thus in reduction from larger micron size anhedral clusters to low and sub-micron size pseudo cubic type particles, grinding energy requirements are comparatively low as the mineral is highly friable. Grades of various particle size distributions are usually accomplished by air separation. Also, the low micron sized pseudo cubic particles exhibit cleavage planes which are clean and smooth. These cleavage planes appear to be largely those forming on angle of intersection which is similar or parallel to one of the interfacial angles of quartz, which equals 85° and 46 minutes.

The unique physical profile of the novaculite particle coupled with a low oil adsorption factor (17 to 20%) more than likely accounts for the unique rheological phenomena exhibited by this mineral. High extender/fillerto-resin ratios are successfully used with but minimal increase in the viscosity, or change in the desired chemical specifications or requirements. Novaculite is extremely wettable, and therefore mixes easily. Utilization of present systems results in the production of processed material in which there is absence of moisture. The material is regarded as hydrophillic, but not as hygroscopic.

Altered novaculite is a solid crystalline substance formed by a three-dimensional arrangement of atoms. The SiO_2 tetrahedra is formed by three dimensional networks of continuous Si-O-Si-O , etc., bonds. This continuous linkage is broken at a surface whether the break occurs at the terminal of a crystal face, or as a result of scratching, fracturing or pulverization. In any event a break will cleave across a great many Si-O bonds leaving unsatisfied atoms. These broken bonds will combine with water (HOH) in various forms and create surface oxides called silanols. It is the silanol (SiOH) which is at this time a subject of considerable interest in several camps. There is reason to believe that the silanol functionality of altered novaculite creates a semi-reinforcing filler, and also makes it an excellent candidate for surface treatment.

Low micron size altered novaculite is a mineral for the extension of the rubber. In this industry altered novaculite is referred to as semi-reinforcing, and is preferred as "gets lost in a hurry".

Altered novaculite finds dramatic

acceptance in the epoxy areas where good rheological flow, heavy loading, and low abrasive coefficient are called for. Delicate electronic encapsulation and application via the epoxy systems call many times for the novaculite as the pure, inert, and excellent dielectric constant filler.

Breakthrough and acceptance of altered novaculite as a "filled foam" extender in the flexible polyurethane field has been accomplished.

The most exciting consideration at this time is the mineral's initial acceptance as a sizable percentage loader or extender in translucent PVC films and sheeting. Due to good rheological flow, low abrasion, purity, and inertness and low refractive index, this area is being exploited by several producers and processors. Other areas of usage include phenolics, polyester, anti-blocking agents, sophisticated polymer films and coatings, latex grouts, rubber mold release agents, etc.

Other fillers

The addition of barium ferrite yields composites with magnetic properties. X-ray opaque products are obtained by the addition of barium sulfate to polyvinyl chloride and other thermoplastic resins.

Boron filaments are strong, light in weight, and much stiffer than aluminum or glass filaments. The commercial product, with six times the modulus of glass fibers, is produced by the deposition of boron from a boron trichloride-hydrogen mixture on a hot tungsten filament similar to that used in incandescent lamps. The diameter of the tungsten core is 0.5 mils and that of the composite is 3-5 mils. The uniformity of adhesion of such resins as epoxy to the boron surface may be improved by etching with nitric acid.

Zinc oxide is used both as a vulcanization promoter and as a filler in rubber. Aluminum, magnesium, and titanium oxides have also been used as reinforcing agents for elastomers and plastics materials. The composites made from these fillers are characterized by increased stiffness, hardness and resistance to creep. Alumina coated silica filaments have been used to reinforce epoxy resins.

The improvement of thermoplastics by reinforcement is not as impressive as in the case of elastomers and other thermosetting resins. However, the improvements are sufficient to justify reinforcement and increase the use of thermoplastics as engineering materi-

als. Since reinforced polymers are essential for progress in the space age, continued improvement in both technology and utility of plastics composites may be anticipated.

More information may be located by consulting the Subject Index, p. 5, the Directory Index at the back of the book, and the following references:

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